

# e-h Coherence and Charging Effects in Ultrasmall Metallic Grains

S. Drewes and S.R. Renn

*Department of Physics, University of California at San Diego, La Jolla, CA 92093*

F. Guinea

*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain*  
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We consider a model for electron tunneling between a pair of ultrasmall metallic grains. Under appropriate circumstances, non-equilibrium final state effects can strongly enhance tunneling and produce electron-hole coherence between the grains. The model displays a quantum phase transition between a Coulomb blockaded state to a coherent state exhibiting subohmic tunneling conductance. The critical state of the junction exhibits a temperature independent resistance of order  $h/e^2$ . Finally we discuss the possible relevance to granular materials and quantum dots. In particular, similarities between the quantum transition in our model and the metal-insulator transition in granular wires observed by Herzog *et al.* are described in detail.

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Recent work by Herzog *et al.* [1] have found dramatic evidence for an unusual metal insulator(MI) transition in granular wires fabricated by *in situ* deposition through a metallic stencil onto a GaAs substrate. The transition involves an abrupt multi-order change in wire resistance as a function of the amount of deposited metal. The transition occurs in a variety of materials (including Sn, Pb, Au, Ag, and  $\text{Pb}_{0.85}\text{Bi}_{0.15}$ ). Although the transition may be observed in wires as wide as 7000Å, the resistance gap decreases with increasing wire width and is absent in two-dimensional films.

In this paper, we wish to consider the possibility of modeling the above behavior in terms of a pair of metallic grains in close proximity. Our model will include two ingredients. The first is electrostatic charging effects. This should be important in the Herzog *et al.* experiments since the charging energy  $E_Q$  is estimated [2] to be large (100K). The second ingredient is a non-equilibrium final state effect in which electrostatic fields between the two particles are suddenly switched on during the tunneling process. This effect is an exciton effect in which the tunneled electron is attracted to the positively charged counter-electrode. We will show that the competition between the exciton effect and Coulomb blockade gives rise to a MI transition between a phase exhibiting sub-Ohmic  $I(V)$  characteristics to a phase exhibiting a Coulomb blockade. The critical state separating these two phases exhibits a temperature independent conductance. Finally, we will discuss the the similarities between these results and those of Herzog *et al.* [1].

We begin our discussion by considering a pair of identical metallic grains on an insulating substrate (see Fig. 1). The grains are in close proximity and form an ultrasmall tunnel junction with intergrain capacitance  $C < 10^{-15}\text{F}$  (For the present argument, we will neglect the intragrain capacitance). The two grains may be part of a granular host. However, tunneling to other grains in the host ma-

terial will be ignored. Now consider a tunneling process in which an electron tunnels from grain #1 to grain #2 (see Fig. 1c-1d). In the classical Coulomb blockade picture a tunneled electron causes all energy levels in the grain #2 to up-shift by  $e^2/2C$  and all energies in grain #1 to down shift by  $e^2/2C$ . In the diagram, we have represented the electrostatic potentials and surface confinement potential as a square well whose shape is unaffected by the tunneling process. Notice that the classical Coulomb blockade picture does not properly describe the non-equilibrium effect associated with suddenly switching on the electrostatic attraction between the two grains (see Fig. 1e-1f). Such effects can give rise to shake-up (orthogonality catastrophe) effects which can seriously effect tunneling rates [3,4] especially in small particles. To see how important these effects might be, consider the classic problem of the x-ray absorption edge [5,6]. In that problem, the absorption intensity, near threshold, could vanish at threshold due to the orthogonality catastrophe [6] or could exhibit a power law divergence known as the exciton effect [5]. *A priori* one might expect that a similar effect could cause the differential conductance of a tunnel junction to vanish or diverge.

To examine these effects in detail, we consider a model [7,3,8,4] which describes tunneling between the two grains,

$$H = H_L + H_R + H_T + \frac{Q^2}{2C} \quad (1)$$

where  $H_T = \sum_{kp} [T_{kp} e^{i\phi} c_k^+ c_p + \text{h.c.}]$  and where  $\phi$  is defined in terms of the voltage difference  $V_L - V_R$  across the grains via the relation  $\phi = e(V_L - V_R)/\hbar$ . Finally, the  $H_L$  and  $H_R$  are given by

$$H_\alpha = \sum_k \epsilon_{k,\alpha}^0 c_{k\alpha}^+ c_{k\alpha} + Q \sum_{kk'} V_{kk'}^\alpha c_{k\alpha}^+ c_{k'\alpha} \quad (2)$$

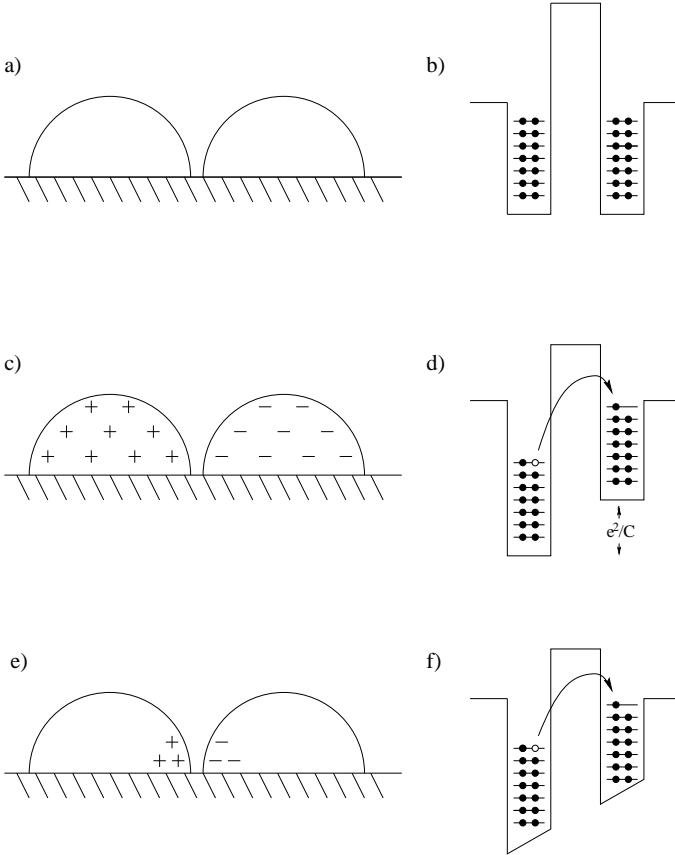


FIG. 1. (a) An illustration of two nearby metallic grains on an insulating substrate. The two grains form an ultrasmall tunnel junction. Although the grains may be part of a composite granular material, coupling to other grains in the host material will be ignored. (b) Energy levels and confinement potential associated with (a). (c) Metallic grains after tunneling event. An unrealistic charge distribution is obtained when  $V_{kk'}^\alpha$  is set to zero. (d) The energy levels and confinement potentials associated with (d). (e) Metallic grains after tunneling event. Charges localized at the tunneling site give rise to long range electrostatic interactions which act as a suddenly switched-on potential  $V_{kk'}^L = V_{kk'}^R$ . (f) The non-equilibrium energy levels and confinement potential associated with (e).

where  $V_{kk'}^\alpha$  represents the sudden change of surface and electrostatic potentials on grain  $\alpha = L, R$  which occurs during the tunneling process. If  $V_{kk'}^\alpha = 0$ , we recover the standard model [7] (see Figs. 1c-1d and 2a) which describes the effects of particle hole excitations induced by tunneling processes in ultrasmall tunnel junctions.  $V_{kk'}^L = V_{kk'}^R \neq 0$  would be chosen to include shake-up and other final state effects in symmetric tunnel junctions.

Now consider the zero temperature tunnel conductance to leading order in  $T_{kp} = T$ . One may calculate the tunneling current using  $I = -2e\text{Im}\{X_{ret}(-eV)\}$  where  $X_{ret} = |T|^2 \int_0^\infty d\tau G_R^e(\tau)G_L^h(\tau) \exp i\omega\tau$  is the retarded response function associated with the non-equilibrium production of the R-electron and L-hole. Now the non-equilibrium electron and hole propagators associ-

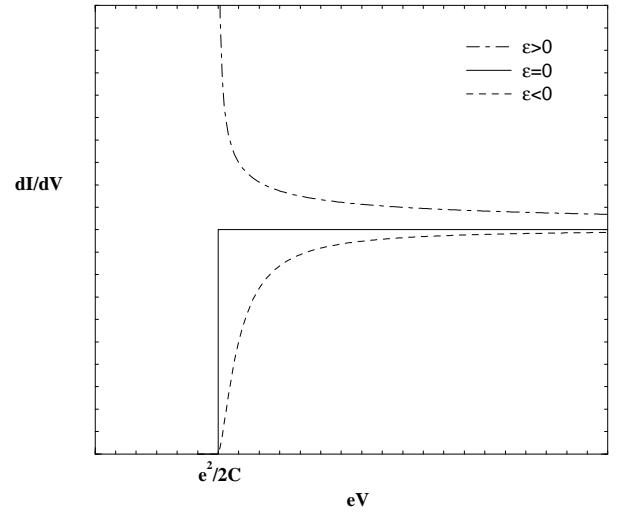


FIG. 2. Differential conductance for  $\epsilon < 0$  (dot-dashed),  $\epsilon = 0$  (solid) and  $\epsilon > 0$  (dashed).  $\epsilon > 0$  curve assumes exciton effect dominates the orthogonality catastrophe.

ated with the suddenly switched on  $V_{kk'}^\alpha$  are given by  $G_R^{h,e}(t) \propto N_R t^{-(1+\delta_R/\pi)^2} \exp -iE_f^R t$  where  $N_\alpha$  is the DOS at the Fermi level in the  $\alpha = L, R$  electrode and  $\delta_\alpha$  is a phase shift associated with the scattering of electrons off the potential  $V_{kk'}^\alpha$ . In the above result, + is used for hole and - for electrons in the right electrode. Similarly  $G_L^{h,e}(t) \propto N_L t^{(1+\delta_L/\pi)^2} \exp -iE_f^L t$  for the left electrode. Because of intergrain charging energy, the electrons tunnel to a non-equilibrium state characterized by Fermi levels shifted such that  $E_f^R - E_f^L = e^2/2C$ . Combining these results one obtains  $\frac{dI}{dV} \propto \frac{1}{R_T} \left( \frac{e^2/C}{eV - e^2/2C} \right)^\epsilon$  where  $\epsilon = 2(\delta_R/\pi + \delta_L/\pi) - (\delta_R/\pi)^2 - (\delta_L/\pi)^2$  and  $R_T^{-1} = 4\pi e^2 N_L N_R |T|^2$ . For small positive  $\delta_\alpha$ , there is a competition between excitonic effects associated with  $2(\delta_R/\pi + \delta_L/\pi)$  and orthogonality effects associated with  $-(\delta_R/\pi)^2 - (\delta_L/\pi)^2$ . Depending on which terms dominate, one can obtain (Fig. 2b) a divergent differential conductance [9] at threshold  $V_T = e^2/2C$  or (Fig. 2c) a vanishing conductance at threshold.

In general the form of the final state interactions  $V_{kk'}^\alpha$  is not important to the following discussion and is difficult to calculate. However there are several observations which can be made: First we observe that one can estimate [10,11]  $|\delta_{L,R}| \sim \pi/k$  where  $k$  is the number of transverse channels available for intergrain tunneling. Next, we observed that  $\delta_R$  will be positive if  $V_{kk'}^\alpha$  is a potential which tends to keep the tunneled electron in the electrode near the tunneling site *i.e.* if the electron is attracted to the positively charged electrode. Similarly  $\delta_L$  will be positive if the hole is attracted to the negatively charged electrode. Hence the electrostatic interaction between a pair of grains with a small number of accessible tunneling channels is expected to give a positive  $\delta_\alpha$  large enough

to make exciton effects observable.

To some readers it may be surprising that the repulsive Coulomb interactions would enhance tunneling between the grains. The behavior is not unusual and can be found in several simple models. For instance, consider a pair of semi-infinite 1-D spinless chains described by the Hamiltonian  $H = [t' c_{L0}^+ c_{R0} + h.c.] + \sum_{i=0} [t c_{Li+1}^+ c_{Li} + h.c.] + U(c_L^+(0)c_L(0) - 1/2)(c_R^+(0)c_R(0) - 1/2)$ . This model is equivalent to a 1-D Anderson impurity model. The inter-chain tunneling is associated with a transverse magnetic field acting on the impurity. For  $U > 0$  the magnetic susceptibility and transverse magnetization  $\langle c_L^+ c_R \rangle$  will be rapidly enhanced with increasing  $U$ . Hence, the differential tunneling conductance will be significantly increased by a large positive  $U$ .

The above discussion of the exciton effect has been performed to leading order in  $|T|^2$ . We will now go beyond leading order in  $|T|^2$  and show that if  $|T|$  large and  $\epsilon > 0$ , that the Coulomb blockade is destroyed. To do this, we integrate out the particle-hole excitations within the grains. This gives an effective action in imaginary time of the form

$$S = \int_0^{\beta\hbar} d\tau \frac{C}{2e^2} \dot{\phi}^2 + \tau_Q^{-\epsilon} \int_0^{\beta\hbar} d\tau d\tau' \alpha(\tau - \tau') [1 - \cos(\phi(\tau) - \phi(\tau'))]$$

where  $\alpha(\tau) = \alpha_0 \left( \frac{\pi k_B T}{\sin(\pi k_B T \tau)} \right)^{2-\epsilon}$  and  $\alpha_0 = \hbar/(2\pi e^2 R_T)$ .

This is a one-dimensional XY model with long range interactions. This model had been studied within the framework of the renormalization group by Kosterlitz [12] who found an order-disorder transition at  $\alpha_0 = \alpha_c = 2/(\epsilon\pi^2)$  for  $\epsilon \geq 0$ . The model is disordered for  $\epsilon \leq 0$  although the absence of an ordered phase when  $\epsilon = 0$  was a source of controversy. [13–15].

In order to understand the nature of the two phases, we calculated the conductance of the model using the Kubo formula  $G(\omega) = \langle |I_t(\omega)|^2 \rangle / \omega$  where  $I_t(\omega)$  is the tunneling current. To leading order in an expansion in powers of  $1/\alpha$ , a spin-wave calcualtion reveals that

$$G = \frac{2\sqrt{\pi}\alpha_0}{R_Q} \frac{\Gamma((1+\epsilon)/2)}{\Gamma(1+\epsilon/2)} \left( \frac{E_Q}{\pi k_B T} \right)^\epsilon \quad (3)$$

where  $E_Q = e^2/2C$  and  $R_Q = \hbar/e^2 = 4.11k\Omega$ . We see that  $G$  diverges at  $T \rightarrow 0$ . Hence one identifies the ordered phase as subohmic. One can also calculate the conductance to leading order in  $\alpha_0$ . In this case one finds  $G \sim \frac{\alpha_0^2}{R_Q} \left( \frac{\pi k_B T}{E_Q} \right)^{2(1-\epsilon)}$  which vanishes as  $T \rightarrow 0$  indicating that the disordered phase is insulating.

To understand the transition in greater detail, we have evaluated the DC conductance using a Monte Carlo simulation [16]. Using [14]

$$G = \frac{2\pi\alpha_0}{\hbar\beta R_Q} \int_0^{\hbar\beta} \gamma_\epsilon(\tau) \langle \cos(\phi(\tau) - \phi(0)) \rangle d\tau \quad (4)$$

where  $\gamma_\epsilon(\tau) = [\pi(k_B T/E_Q)/\sin(\pi k_B T \tau \hbar)]^{-\epsilon}$ , we evaluate  $G$  using  $\langle \cos(\phi(\tau) - \phi(\tau')) \rangle$  obtained from a series of simulations including  $10^5$  cycle runs for the 10, 20, and 32 timeslice systems and  $2 \times 10^5$  cycle runs for the 64 and 128 timeslice systems. The results for  $\epsilon = 0.2$  are presented in Fig. 3. The transition between the sub-Ohmic (high  $\alpha_0$ ) phase to the insulating (low  $\alpha_0$ ) phase is evident. Interestingly one observed the conductance curves cross at a single point. This point identifies a transition at a critical value of  $\alpha_c = 0.9$  which compares well to  $\alpha_c = 1.01$  obtained by Kosterlitz RG treatment.

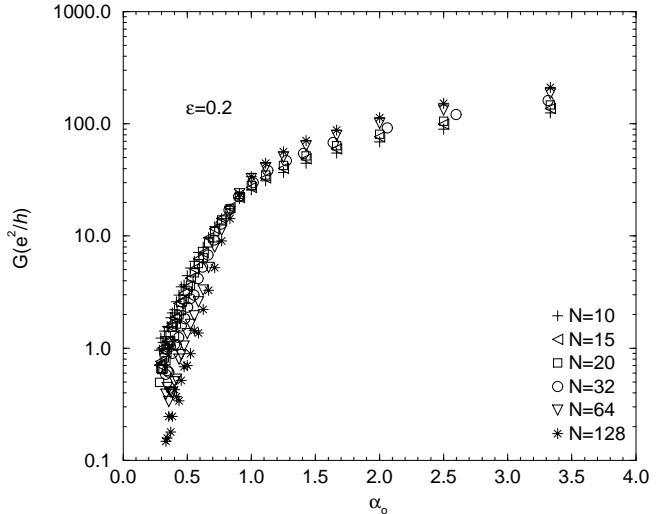


FIG. 3. Conductance obtained from a MC simulation. Notice,  $G(\alpha_0)$  curves intersect at  $G_c \approx 11e^2/h$ . This suggests that the conductance of the critical state is a universal, temperature independent constant.

The fact that curves intersect at all indicates that  $\alpha_c$  separates metallic from insulating behavior. However, the observation that all line cross at  $G_c \approx 11\frac{e^2}{h} \approx 1/(2.3k\Omega)$  seems to indicate that the critical state has a finite temperature independent conductance. The existence of a critical state with a finite resistance can be understood as follows. In general, finite size scaling theory implies that the critical states exhibits correlations of the form  $\langle \exp i\phi(\tau) \exp -i\phi(0) \rangle = \left( \frac{\tau_Q}{\tau} \right)^{d-2+\eta} F(\hbar\beta/\tau)$  where  $\tau_Q = \hbar/E_Q$  is the width of the time slices,  $d = 1$  is the space-time dimensionality, and where  $F(x)$  is a universal scaling function which is finite as  $x \rightarrow 0$ . According to Fisher, Ma and Nickel [17],  $\eta = 1 + \epsilon$  is exact for our model. It follows that

$$G_c = b(\epsilon) \frac{e^2}{h} \quad (5)$$

at criticality. Since the DC conductance depends only on the  $\omega \rightarrow 0$  limit of the model, the above result is a universal but  $\epsilon$  dependent result. Typically simulations for other values of  $\epsilon$  reveal that  $1/G_c \sim 10^5 \Omega$  except in

the  $\epsilon \rightarrow 0$  limit where  $G_c \rightarrow \infty$ . It should be mentioned that the Herzog data reveals that the highest resistance metallic state in Au (width: 400 Å), Pb<sub>0.85</sub>Bi<sub>0.15</sub> (width: 575 Å and 850 Å), and Sn (width: 550 Å) wires have critical resistances of  $2k\Omega$ ,  $2k\Omega$ ,  $4k\Omega$ , and  $4k\Omega$ , respectively. Such values of  $G_C^{-1}$  are consistent with eqn. 5.

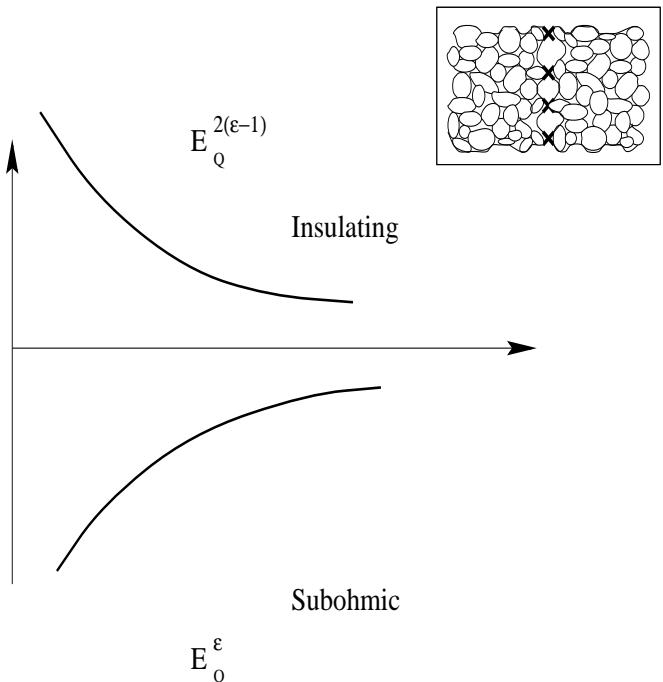


FIG. 4. Modeling a crack as a series of parallel tunnel junctions (see inset). Observe that the charging energy decreases with increasing wire width. The decreasing  $E_Q$  causes the resistance gap to close and the resistance of non-critical subohmic wires to increase.

*Discussion* – We wish to consider the relevance of our tunnel junction to the MI transition observed by Herzog *et al.* [1]. Herzog's MI transition occurs in many different materials and exhibits a resistance gap which depends on the wire width, 500 Å – 6000 Å. This suggests that the transition does not involve some microscopic phenomenon in the interior/surface of the grains but, instead, involves some low energy collective behavior which requires two or more grains. In addition, it appears that the MI transition is not a percolation transition in which the drop in the resistance is determined by purely geometrical considerations such as number of parallel connections spanning a backbone cluster. This is clear since percolation transition can occur in films but not in wires. At this point, one might model the wire as a disordered network of tunnel junctions where Coulomb blockade effects could produce an insulating phase. This is reasonable since charging energies are estimated [2] to be  $\sim 100K$ . Assuming the tunnel junction conductances to be broadly distributed, the wire resistance will be dominated by the tunnel junctions with highest resistance [18].

Now consider the dependence of the wire resistance on

the wire width. Let  $l_\phi$  be the phase coherence length *i.e.* the length scale that correlations  $\langle e^{i\phi(\vec{r})} e^{-i\phi(0)} \rangle$  die off in the disordered phase. Then for wire widths  $w \ll l_\phi$ , the low frequency behavior of the obstruction will be described by the tunnel junction model with a charging energy which decreases with increasing wire width. For instance, in a narrow wire ( $w \ll l_\phi$ ) phase difference across multiple tunneling sites spanning a crack or weak-link will be equal. (See fig. 4.) Hence, the capacitances comprising the weak-link add in parallel. This is a useful observation since the decreasing charging energy associated with increasing wire width will cause the resistance of the non-critical subohmic states to increase like  $(T/E_Q)^\epsilon$  (eq. 3) similar to the behavior observed by Herzog *et al.*. The increase of the metallic wire resistance with wire width is a unique phenomenon which is difficult to obtain from alternative models. The model also predicts that the resistance of insulating wires will *decrease* with increasing wire width. Consequently the resistance gap will decrease until  $w \sim l_\phi$  where the crossover to two dimensional transport will occur.

At this point, we should mention that our model makes several predictions which have not yet been tested. First, from the Kosterlitz RNG treatment demonstrates the existence of a characteristic energy scale,  $\Delta = E_Q(1 - \alpha_0/\alpha_c)^{1/\epsilon}$ . This behavior should be detectable by examining the differential conductance which obeys a scaling ansatz of the form  $dI/dV = \frac{e^2}{h}(eV/E_Q)^\delta F(eV/\Delta)$  where  $\delta = 0$  in order that scaling ansatz is consistent with eq. 5. The second prediction is that the transition to the phase coherent state in arrays of coupled tunnel junctions will be accompanied by a divergence in  $l_\phi$ . This unique behavior should be readily observable in magnetoresistance measurements performed on insulating granular wires.

We should also mention that one should also be able to search for the subohmic to insulator transition in double quantum dot systems of the sort considered by Waugh *et al.* [19,20]. The double-dot systems have several useful features including (1.) a small number of tunneling channels which implies the large phase shifts [10] required for an exciton effect, (2.) small intergrain capacitances [19], and (3.) precise control of the tunneling barrier between dots. Unfortunately, the Waugh experiment itself could not distinguish between a cross-over and a phase transition. However, this is not an inherent limitation of the experimental method. So an attempt to search for this quantum phase transition in the double dot should be feasible and would certainly be most welcome.

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